

Hydrogen Getters for Use in the TRUPACT-II

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October 2000

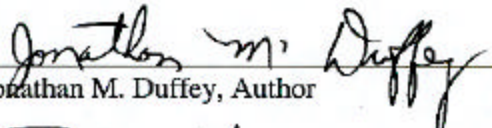
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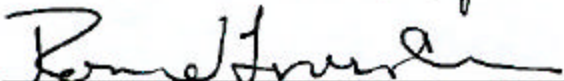
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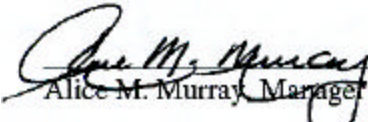
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Acknowledgements

The authors would like to acknowledge the following individuals for their assistance in completing various aspects of this work: Mark Crowder, Bob Pierce, and Kit Heung of the Savannah River Technology Center, Aiken, South Carolina; Tim Shepodd of Sandia National Laboratory, Livermore, California; Bradley Phillip of Vacuum Energy, Inc., Cleveland, Ohio; and Paul Nigrey of Sandia National Laboratory, Albuquerque, New Mexico.

Executive Summary

This report provides a detailed review of SRTC results obtained under Phase 1 testing of the Transuranic and Mixed Waste Focus Area's (TMFA's) Hydrogen Gas Getters Evaluation. The results of this initial evaluation demonstrate that hydrogen gas getters meet the requirements proposed for transportation of transuranic (TRU) wastes in the Transuranic Package Transporter-II (TRUPACT-II). Recommendations for the Phase 2 efforts to enhance hydrogen getter performance and to complete additional testing are provided. These recommendations are intended to support eventual design and deployment of a hydrogen getter "system" that will be approved by the Nuclear Regulatory Commission (NRC) for use in shipping TRU wastes.

This evaluation reviews the test results for two hydrogen getter materials. The original material proposed for testing as part of the TMFA Hydrogen Gas Getters Evaluation program is a composite called sol-gel metal hydride (SGMH). The effectiveness of SGMH is compared to a second getter material that has been tested for use at the Savannah River Site (SRS) to support transportation of legacy nuclear materials. This alternate getter material meets all of the TMFA requirements and offers several advantages over SGMH including greater hydrogen capacity, ability to maintain lower hydrogen pressures at elevated temperature, and greater resistance to poisons. Based on our experience with these two getter materials, we recommend this alternate material for enhancement during Phase 2 of this program.

The alternate getter material presented in this report is a commercial product manufactured by Vacuum Energy, Inc. (VEI) under exclusive license from Sandia National Laboratory (SNL). The material is described in detail by U. S. Patent Numbers 6,063,307 and 5,837,158. Currently, it is used commercially to scavenge hydrogen gas in applications where the presence of hydrogen is undesirable. Examples of such applications include vacuum insulation panels, heat transfer pipes, and batteries. We are currently communicating with SNL and VEI about developing and testing enhancements of this material that may provide additional advantages as part of an engineered component in the TRUPACT-II.

Introduction

This document reports on Phase 1 testing conducted at the Savannah River Technology Center (SRTC) for the use of hydrogen getters in the TRUPACT-II. This work was undertaken in response to the Hydrogen Gas Getters Evaluation Program Request for Proposals issued by the TMFA.¹ The purpose of Phase 1 testing was to demonstrate a hydrogen getter capable of satisfying the getter requirements listed in a Statement of Work (SOW) which accompanied the Request for Proposals.

Background

The decomposition of TRU waste, resulting from the interaction of radiation with various waste components, produces non-radioactive gaseous by-products. Additional gases and vapors (e.g., methane and trichloroethylene) may be present in sealed TRU waste containers from other sources, such as volatilization of waste content and thermal or biological degradation of waste components. The headspace of TRU waste drums has been shown to include gases and vapors such as hydrogen, oxygen, carbon dioxide, carbon monoxide, methane, trichloroethylene (TCE), hydrogen chloride, and acetone.^{2,3,4,5} The accumulation of hydrogen within the individual waste packages and drums, as well as within the sealed TRUPACT-II inner containment vessel (ICV), presents a safety hazard. The Safety Analysis Report for the TRUPACT-II Shipping Package (TRUPACT-II SARP)⁶ limits the hydrogen concentration to less than 5% by volume to avoid forming flammable or explosive gas mixtures.

A 40-Watt (40-W) limit has been placed on the overall radioactive decay energy of the TRUPACT-II contents, based on the ability of the TRUPACT-II package to dissipate the decay heat. However, the character of TRU waste matrices and the energy of some radioactive contaminants prevent the TRUPACT-II from being loaded to the full 40-W limit because the amount of hydrogen produced could exceed the 5% limit. The amount of hydrogen generated is a function of both the waste type and the decay energy; therefore, operating limits for allowable radioactive decay energy in the TRUPACT-II have been established for different waste types. For wastes contaminated with Pu-238, which decays at about 0.5 W g^{-1} , the total TRUPACT-II loading may be limited to only 3 W, or 6 g Pu-238.

The current SRS waste inventory includes about 7000 drums of Pu-238-contaminated waste, with more than half of these containing greater than 6 g of Pu-238.⁷ Needs for technologies to prevent hydrogen accumulation in the TRUPACT-II exist at other sites within the Department of Energy (DOE) that have high-wattage level wastes. The needs include Pu-238 waste at LANL and americium/curium wastes at Hanford, INEEL, ORNL, and RFETS. Due to current decay energy operating limits, drums of this type of waste cannot be shipped without repackaging to decrease the overall decay energy per drum. This restriction will ultimately result in more shipments and higher transportation costs per waste drum or treatment of the waste to reduce the hydrogen generation rate.

To address this problem, a request for proposals was issued for the development of technologies to mitigate hydrogen accumulation in the TRUPACT-II and evaluation of alternative options for TRU packaging. The DOE's TMFA and Carlsbad Area Office (CAO) are working to reduce the costs of transporting TRU waste by developing technologies that will take advantage of the full 40-W decay energy limit for the TRUPACT-II.⁸ If successful, the need for repackaging will be minimized and the number of waste shipments reduced.

Two complementary approaches to increasing the TRUPACT-II wattage limits are being taken. The first approach is to package the waste in a way that minimizes the number of confinement layers and

allows hydrogen to diffuse out of individual packages and drums and into the ICV of the TRUPACT-II. This approach will allow waste limits to be calculated based on hydrogen concentration in the minimum void volume of the ICV (i.e., 2450 L for a 14-drum payload).⁶ The second approach is to remove hydrogen from the ICV by reaction with or absorption by another material. This removal step is referred to as “gettering” hydrogen. Use of an appropriate getter material to remove hydrogen from the ICV as it is generated should enable the hydrogen concentration to be kept below the 5% lower explosive limit.

The performance requirements for a getter deployed in the TRUPACT-II depend on getter deployment location (i.e., within each waste drum or within the ICV).¹ If deployed in each drum, the getter must be capable of removing hydrogen at a maximum rate of $8.8 \times 10^{-7} \text{ mol s}^{-1}$ for a period of 365 days. An operational life of 365 days is required to account for both on-site storage and shipping time after repackaging. If deployed in the ICV, the getter must operate for 60 days and maintain a maximum gettering rate of $1.2 \times 10^{-5} \text{ mol s}^{-1}$. In addition to operational life, the SOW lists a number of other getter issues and requirements including the impact of poisons on getter performance, compatibility of the getter with chemical contents of the payload, the operating temperature and pressure ranges of the getter, the potential for reversible hydrogen absorption, the potential for generation of free liquids by the getter, the effect of radiation on getter performance, and the potential temperature effects of the gettering reaction(s) on the payload. In addition, the getter must function as a passive system with no external energy source supplied.

In a recent evaluation of getter materials for use in the TRUPACT-II,⁹ we recommended the implementation of a composite getter material to mitigate the effects of poisons and expand the capability of hydrogen getter materials. Based on initial screening tests conducted with a patented hydrogen storage material¹⁰ developed by SRTC, we proposed a class of getter materials called composite metal hydrides for the removal of hydrogen from the TRUPACT-II. The proposed materials are discussed in the following section.

Technology Description

The term “metal hydride” is commonly used to refer to a metal or metal alloy that reacts reversibly with hydrogen. Metal hydrides have been studied and used for purposes of hydrogen separation and storage for some time.¹¹ In general, metal hydrides absorb hydrogen at lower temperatures and desorb hydrogen at higher temperatures, although the functional temperature range varies widely for different metal hydrides. The fact that the reaction is reversible suggests metal hydrides used as hydrogen getters in the TRUPACT-II could be recycled and reused, potentially resulting in significant savings in the costs associated with transporting TRU waste.

When metal hydrides are exposed to certain gases called poisons, the absorption of hydrogen is reduced or prevented altogether. Also, repeated absorption and desorption of hydrogen causes metal hydride particles to break down (decrepitate) into micron-size fines, which can lead to a number of engineering concerns. In an attempt to address these problems, a composite getter material called sol-gel metal hydride (SGMH) was developed at SRS.¹² [Note: The term composite metal hydride (CMH) may be used to indicate either sol-gel metal hydride or other composite metal hydrides developed within SRTC. The specific formulations of these materials are not disclosed.]

SGMH consists of particles of metal hydride (typically less than 50 μm) encapsulated in a porous silica-gel matrix formed by a sol-gel process. The resulting product is typically crushed or ground into particles 1-5 mm in size. The pore sizes of the SGMH particles are large enough to permit hydrogen to enter the matrix, but small enough to restrict or prohibit the passage of larger molecules

such as oxygen and carbon monoxide that could poison the metal surface. Tests on SGMH indicate the encapsulated metal absorbs hydrogen reversibly just as the unencapsulated sample does. Also, after 100 absorption/desorption cycles the metal hydride particles are retained within the silica matrix thus eliminating engineering concerns associated with the production of micron-size metal particles.¹²

CMH samples have been prepared by encapsulating metal hydride particles into a porous silica matrix or other matrix materials to create a composite form. In previous tests, these composite getters have been shown to provide partial protection to the active metal surface from small poison molecules such as oxygen (air) and carbon monoxide.¹² Thus, the protective mechanism was expected to protect from larger poison molecules as well. Following exposure to air for a period of several days or more, hydrogen absorption rates for CMH are as much as 10 to 100 times greater than for the unprotected metal. In addition, the composite getters have been shown to absorb hydrogen across the required temperature range.

Of the metal hydrides we have evaluated for preparation of composite getter materials, two have shown the most promise— NdCo_3 and $\text{LaNi}_{4.0}\text{Al}_{1.0}$ (LANA1). Initial tests were conducted on small, gram-size batches of LANA1 SGMH, LANA1 CMH, and NdCo_3 CMH. For Phase 1 testing, we attempted to scale-up preparation of these three composites to obtain sufficient sample for testing; however, the scale-up preparations of LANA1 CMH and NdCo_3 CMH were not successful. Therefore, of the three composite metal hydride candidates, only LANA1 SGMH was included in this test program.

As part of a parallel effort involving hydrogen mitigation for on-site packaging and transportation at SRS, we identified and began investigating a commercially available hydrogen getter (Vacuum Energy, Inc., Cleveland, Ohio). This getter, which we refer to as VEI getter, consists of a mixture of organic polymers containing carbon-carbon double bonds and a palladium catalyst on a carbon support.¹³ In the absence of oxygen, hydrogen is removed by reaction with the carbon-carbon double bonds (i.e., hydrogenation)). When oxygen is present, VEI getter functions as a recombination catalyst until the oxygen is consumed, then proceeds by the hydrogenation mechanism. In initial tests, this material demonstrated very favorable hydrogen gettering characteristics relative to the anticipated requirements for the on-site transportation application, as well as those for the TRUPACT-II. Therefore, applicable test results for VEI getter will be presented in this report along with test results for LANA1 SGMH.

Experimental

Materials and Apparatus

LANA1 (Japan Metals, Ltd.) was obtained in the form of granules less than about 1 mm in size (-16 mesh, US standard). The particle sizes were reduced by grinding (in air) to a fine powder using a horizontal ball-mill. The ground metal was passed through a 325-mesh screen to obtain particles less than 45 μm in size. LANA1 SGMH was prepared from the ground LANA1, tetraethylorthosilicate, ethanol, and deionized water according to previously published procedures.¹⁰ After air-drying for several days, the sample (1-mm to 5-mm size pieces) was placed in the gas manifold, gradually heated to 200 °C under vacuum over a period of approximately two hours, cooled to room temperature, and activated by saturating with hydrogen. Following the initial activation, the hydrogen was desorbed by heating to 200 °C under vacuum. This hydrogen absorption/desorption cycle was repeated once more, then the sample was cooled to room temperature, exposed to room air, and immediately transferred from the sample bed to a screw-cap glass vial for storage. Previous studies have shown that improved poison resistance can be achieved by heating SGMH samples in vacuum to about 400 °C to reduce pore size. However, this process also reduces the hydrogen capacity, presumably by completely closing a percentage of the silica pores. To retain maximum hydrogen capacity of the LANA1 SGMH, the SGMH material used in these tests was not heated above 200 °C. We will consider the heat treatment process as a potential enhancement to be investigated in Phase 2.

VEI getter was received from the manufacturer (Vacuum Energy, Inc.) as a coarse black powder. Once received, no special precautions were taken to protect the material from air other than sealing the container when not in use. In addition, no activation step was necessary to initiate hydrogen absorption after exposure to air. The approximate hydrogenation capacity was supplied by the manufacturer and confirmed in our laboratory by experiment.

Solvents used to generate poison vapors for poison tests were reagent grade. Milliliter quantities of each poison liquid were equilibrated with air for several days in sealed, 125-mL glass vessels to obtain poison vapor concentrations in the headspace gas equal to the vapor pressure of each liquid at ambient temperature. The vessels were also equipped with a side-arm stopcock and rubber septum to permit removal of a portion of the gas phase with a gas-tight syringe. Poison exposures were conducted in similar 360-mL glass vessels, also equipped with a side-arm stopcock and rubber septum to allow for removal of air and introduction of an equal volume of poison vapor using a gas-tight syringe. Poison tests were also conducted using a standard gas mixture of 5% CO, 1% CO₂, 5% H₂, 10% N₂, 10% N₂O, and 10% O₂ in argon to achieve the desired concentration of CO in the test vessel.

Figure 1 is a schematic for one of the sections in the gas manifold used in these experiments. This arrangement simplifies the addition of an accurately known amount of gas to the sample. The gas manifold was constructed of stainless steel sample containers and calibrated volumes, 1/4-inch stainless steel tubing, Cajon[®] fittings, and Nupro[®] valves. The sample beds were designed to accept a 4-dram glass sample vial in an upright orientation to facilitate sample introduction and removal. Bed temperatures were monitored by thermocouples (type J or K) inserted into holes drilled into the walls of the beds and extending from the bottom to a point approximately half-way to the top of the beds. The volumes of tubing between valves were calibrated so that known gas volumes could be introduced to the sample chamber.

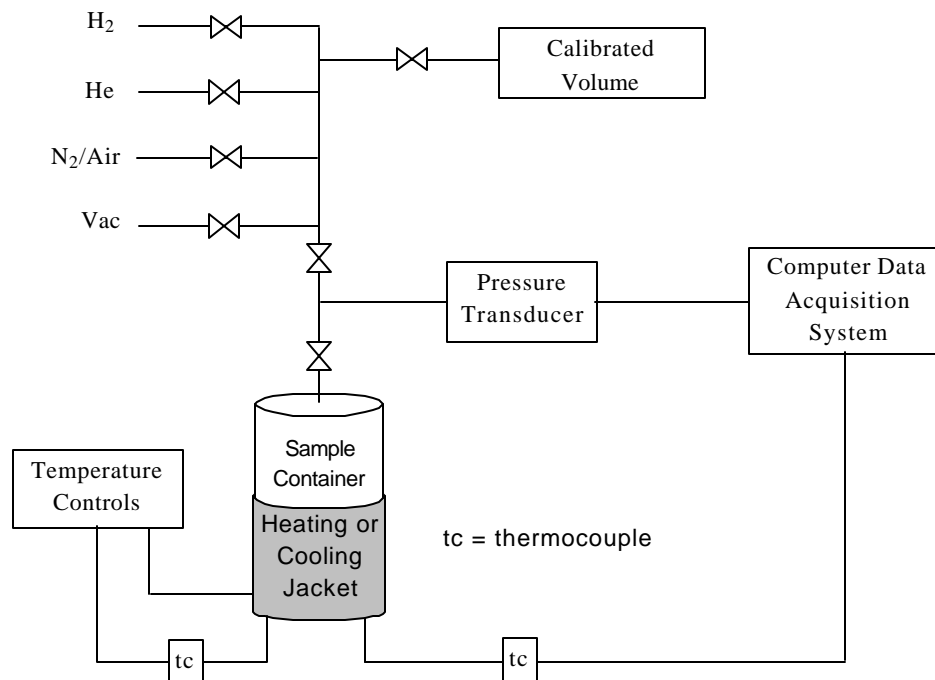


Figure 1. Schematic of hydrogen getter test apparatus.

The gas pressures were measured by MKS Baratron[®] pressure transducers (10,000 torr range; 0.1 torr readability). A Varian millitorr vacuum gauge was also used to measure the manifold pressure when open to vacuum. Electrical resistance heaters fitted to the sample beds and connected to Cole Parmer Digisense temperature controllers were used to heat the sample beds for the experiments at elevated temperature and for desorption of hydrogen from metal hydrides. A Neslab[®] refrigerated circulating bath was used to cool the sample beds for the low temperature experiments. Date, time, temperature, and pressure data were recorded and monitored via LabView[®] computer software.

Test Program

The Statement of Work requires tests of the following parameters:

1. Potential Poisons
2. Compatibility
3. Operating Temperature Range
4. Pressure
5. Reversibility
6. Operational Life
7. Free Liquids
8. Temperature Effect
9. Passive Systems
10. Radiation Effects

Our Phase 1 test program¹⁴ consisted of an evaluation of these parameters as independent variables, but not in combination. That is, the consequences of combined effects (e.g., exposure to potential poisons at elevated temperature) were not evaluated. Issues identified as a result of data review should be addressed as part of the Phase 2 development and expanded testing.

The criteria used to evaluate the performance of getter materials in this work are the hydrogen capacity and absorption (LANA1 SGMH) or hydrogenation (VEI getter) rate. The impact of selected test conditions on rate and, where deemed necessary, capacity was determined for each getter being evaluated. The response of the getter materials to each test condition was used to document getter function. These measurements were initiated by placing the getter material in a fixed volume container and adding hydrogen gas to provide the desired hydrogen concentration at a known pressure and temperature. The resulting pressure drop with time was used to calculate the getter's hydrogen absorption or hydrogenation rate. Figure 2 illustrates this process.

Table 1 gives hydrogen capacities for LANA1 SGMH and VEI getter. The theoretical capacity of LANA1 SGMH was calculated from previous measurements of LANA1 metal capacity at ambient temperature and a hydrogen overpressure of 1000 to 2000 torr, and the LANA1 content of the composite (≈ 37 wt %). The theoretical capacity for VEI getter was supplied by the manufacturer. Because the hydrogen capacity of metal hydrides decreases with increasing temperature, the useful hydrogen capacity (rated capacity) for LANA1 SGMH was estimated from previous hydrogen absorption measurements for LANA1 metal at 160 °F, the maximum operating temperature of the TRUPACT-II. The rated capacity of VEI getter was conservatively estimated at 90% of the theoretical capacity. Based on the rated capacities listed in Table 1, a minimum of 140 kg of LANA1 SGMH or 13 kg of VEI getter would be required to remove the maximum amount of hydrogen (i.e., 62 moles) generated during a 60-day shipping period. These estimated amounts do not take into account hydrogen removed by recombination with oxygen. If oxygen is not consumed by some other mechanism, there is sufficient oxygen to recombine with at least 37 moles of hydrogen, thereby further reducing the required getter capacity.

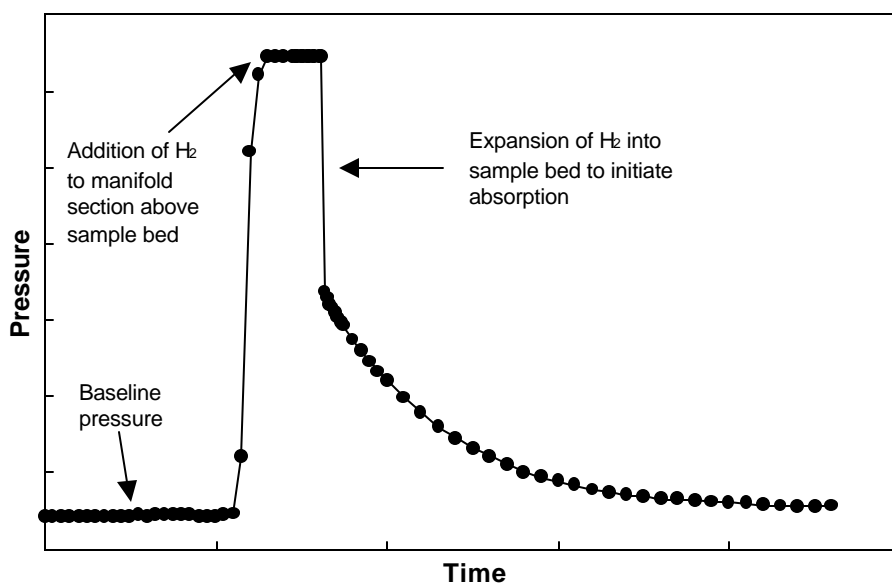


Figure 2. Sample hydrogen absorption curve for a composite metal hydride getter.

Table 1. Hydrogen Capacities of Getter Materials Tested

Getter	Theoretical Capacity (mol kg ⁻¹)	Measured Capacity (mol kg ⁻¹)	Rated Capacity (mol kg ⁻¹)	Amount of Getter Required Based on Capacity Only (kg)
LANA1 SGMH	1.9	1.5	0.45	140
VEI Polymer Getter	5.4	5.9	4.8	13

Rate measurements, and in some instances capacity measurements, were made across the specified range of test conditions required by the SOW. In some cases (e.g., poison concentration), only the extreme conditions were evaluated for impact on getter functions. For other parameters (e.g., temperature and pressure), the getters were tested at minimum, midpoint, and maximum values.

In tests conducted prior to Phase 1, we observed that exposure of freshly activated SGMH to air (i.e., oxygen and/or moisture) led to a significant decrease in hydrogen absorption rate compared to samples not exposed to air. To distinguish the effects of air exposure from the effects of other parameters (e.g., temperature, pressure, etc.), hydrogen removal rates were measured in a nitrogen atmosphere using freshly activated samples of LANA1 SGMH throughout this study. In contrast, exposure to air has no apparent effect on VEI getter performance. Therefore, VEI getter was tested as received (no activation required), and rate measurements were made in a nitrogen atmosphere for comparison with LANA1 SGMH. Both oxygen (air) and moisture were included in the test matrix, and their effects on hydrogen removal rates are discussed in the section on potential poisons. The tests conducted to evaluate each of the parameters listed in the SOW are described in the following paragraphs. A summary of the test matrix is provided in Attachment 1.

Operating Temperature Range

For use in the TRUPACT-II, the hydrogen getter must exhibit hydrogen gettering rates over the temperature range of -20 °F to 160 °F sufficient to prevent the hydrogen concentration from exceeding the 5% limit.¹ Tests were conducted to measure hydrogen absorption or hydrogenation rates in nitrogen at three temperatures: -20 °F, ambient temperature (approx. 70 °F), and 160 °F. The rate measurements were made with samples loaded to approximately 50% of the rated capacity. In each case, the sample was brought to equilibrium at the desired temperature in a nitrogen atmosphere, then hydrogen was added to achieve a concentration of approximately 5% (v/v), and the pressure drop with time was recorded.

Reversibility

In addition to maintaining sufficient rate, the SOW states that “desorption of hydrogen from the getter during the shipping period is not acceptable because it may potentially result in the hydrogen concentration exceeding the 5% limit.” Because metal hydrides absorb hydrogen reversibly, some fraction of absorbed hydrogen will be released as LANA1 SGMH is heated. In other words, the capacity of LANA1 SGMH, as well as other CMHs, decreases to some extent with increasing temperature. This characteristic of metal hydrides and, consequently, of CMHs determines the useful (rated) capacity of a given CMH material. Previous tests with LANA1 indicated that the metal could maintain the hydrogen concentration below 5% when loaded to approximately 30% of its theoretical capacity at ambient temperature and then heated to 160 °F. Therefore, the useful (rated) capacity of

LANA1 SGMH should also be approximately 30% of the theoretical capacity, based on the metal hydride content of the composite. VEI getter functions by irreversible hydrogenation and recombination mechanisms and does not release hydrogen upon heating to 160 °F.

The reversibility of hydrogen absorption for LANA1 SGMH and VEI getter was tested as follows. The getter candidates were loaded to 100% of their rated capacity at ambient temperature, then heated to 160 °F in a nitrogen atmosphere. The pressure rise recorded was compared with that for LANA1 SGMH at zero percentage loading (fully desorbed) in nitrogen in the same sample bed configuration.

Getter Operational Life (Capacity)

We anticipate deploying the getter in the ICV; therefore, the getter must be capable of absorbing hydrogen at a rate of $1.2 \times 10^{-5} \text{ mol s}^{-1}$ for a period of 60 days.¹ Assuming the maximum hydrogen generation rate is maintained for the full 60 days, a total hydrogen capacity of 62 moles is required. To minimize costs, it is desirable to use the smallest amount of getter possible while maintaining sufficient rate and capacity.

Previous tests have shown that hydrogen absorption (LANA1 SGMH) and hydrogenation (VEI getter) rates in a hydrogen-only atmosphere decrease as capacity is consumed (increased loading). Rate has also been shown to decrease when hydrogen is diluted with another gas or gases. To determine the change in absorption or hydrogenation rate with increased loading under more realistic conditions, we measured the rate in nitrogen at three levels of loading—5%, 50%, and 90% rated capacity. This test was accomplished by loading the getter material to approximately 5% rated capacity, then measuring the rate of hydrogen absorption or hydrogenation as a function of hydrogen concentration ($\leq 5 \text{ vol } \%$) in nitrogen. This process was then repeated at 50% and 90% of the getters' rated capacities.

Pressure

A hydrogen getter deployed in the TRUPACT-II must maintain sufficient rate performance in the pressure range from 0 to 50 psig. Tests were conducted to measure hydrogen absorption or hydrogenation rates for a prepared gas mixture of approximately 5% (v/v) hydrogen in nitrogen at 0-, 15-, and 50-psig total pressure. The rate measurements were made with samples loaded to approximately 50% of the rated capacity.

Potential Poisons

Many potential poisons can be present in the TRUPACT-II.^{2,3,4,5} The poisons are grouped into three categories: flammable volatile organic compounds (VOCs), nonflammable VOCs, and inorganics. A few poisons from each category were selected to determine their effect on the getter materials after exposure to approximately 1000 ppm of poison vapor (i.e., two times the maximum anticipated poison concentration) for a period of one week. The representative poisons selected were as follows:

Flammable VOCs: acetone, methanol, and toluene

Nonflammable VOCs: chloroform and tetrachloroethylene

Inorganics: carbon monoxide, hydrogen chloride, and water vapor

The poison tests were conducted as follows:

Poison exposure:

1. The getter material (either 2.00 g of LANA1 SGMH or 1.35 g of VEI) was weighed into a 4-dram borosilicate glass vial and placed into one of the 360-mL poison test vessels described previously.
2. A gas-tight syringe was used to withdraw a calculated volume of air from the poison test vessel.
3. An equal volume of headspace gas was then withdrawn from the desired poison equilibration vessel and injected into the test vessel to give a poison concentration of 1000 ppm in air. The volume of air withdrawn and poison vapor injected differed for each poison (Table 2).^{*} The volume needed was calculated based on the equilibrium vapor pressure¹⁵ of each poison in the poison equilibration vessel at ambient temperature and the volume of the poison test vessel (360 mL).
4. After approximately seven days, the vial of getter material was removed from the test vessel and immediately capped until tested.

In addition to the poison exposures described above, one sample of each getter was exposed to air in one of the 360-mL test vessels with no poison added for approximately seven days. These samples served as the control samples to determine what effect each poison had on getter performance.

Getter performance after poison exposure:

1. The sample vial was uncapped, placed in a sample bed, sealed, and attached to the gas manifold.
2. The manifold line and sample bed were evacuated briefly (a few seconds) to approximately one torr to remove most of the air. Then, the valve to vacuum was closed and the equilibrium pressure in the sample chamber was recorded.
3. Next, the sample bed was isolated and, without further evacuation of the sample chamber, a known amount of hydrogen (≈ 60 torr) was added to the line above the sample bed.
4. The hydrogen was then expanded into the sample bed ($P_{H_2} \approx 30$ torr) to measure rate of hydrogen absorption (LANA1 SGMH) or hydrogenation (VEI getter) in vacuum.
5. After a period of from 4 to 12 hours, the sample chamber was evacuated again very briefly to remove any remaining hydrogen, and approximately 525 torr (0.69 atm) of nitrogen was introduced into the sample chamber. This nitrogen pressure was chosen to be consistent with numerous tests conducted previously in which expansion of one atmosphere (760 torr) of air or nitrogen into the sample container resulted in a total pressure of about 525 torr. Since this pressure is not significantly than the 600 torr of nitrogen that would remain after all oxygen was consumed from one atmosphere of air, we continued to work with 525 torr of nitrogen.
6. Once a stable pressure reading was obtained, hydrogen was added to the sample chamber to measure the rate in nitrogen at ≤ 5 vol % hydrogen.

^{*} The anticipated maximum poison concentration of 500 ppm in the TRUPACT-II is much less than the equilibrium vapor concentration of these representative solvents at ambient temperature. This assumption suggests there can be no free liquid solvent in the package. This test was designed to expose the getter to a concentration and volume of poison vapor that exceed the expected poison concentration and ratio of gas volume to required getter mass for the TRUPACT-II. Therefore, this test is a conservative test of the effect of poison vapors on getter performance.

Table 2. Vapor Pressures and Volumes of Potential Poisons used in Screening Tests

Compound	Vapor Press at 20 °C (torr)	Volume of Gas or Vapor to Give 1000 ppm Poison in Test Vessel (mL)
Acetone	176	1.6
Carbon monoxide	NA ^(a)	7.2
Chloroform	154	1.8
Hydrochloric acid (37%) ^(b)	160	1.7
Methanol	96	2.9
Tetrachloroethylene	14	19.5
Toluene	22	12.4

^(a) CO was added from a standard gas mixture containing 5% CO.

^(b) In this case, due to the vapor pressure of water over 37% HCl (i.e., 2.7 torr at 20 °C), the poison vapor in the test vessel included about 17 ppm water vapor in addition to 1000 ppm HCl.

Free Liquids

In general, generation of free liquids within the TRUPACT-II by the hydrogen gettering reaction is undesirable because no free liquids are acceptable in the ICV under normal transport conditions. Both LANA1 SGMH and VEI getter can function as recombination catalysts to produce water when both oxygen and hydrogen are present. Based on the stoichiometry of the recombination reaction, the maximum amount of water generated will depend on whether oxygen or hydrogen is the limiting reactant. For getter deployment in the ICV, the maximum amount of hydrogen generated is expected to be about 62 moles. If all of this hydrogen reacts with oxygen to form water, approximately 1.1 kg (1.1 L) of water would be formed. The amount of water generated will be less than 1.1 kg if oxygen is the limiting reactant.

Two separate tests were conducted to determine the potential for the getters to generate free liquid. In one test, samples of each getter (0% rated capacity) were stored at ambient temperature and 100% relative humidity to determine the maximum amount of moisture absorbed by each material. Each sample was weighed periodically until a constant weight was attained. The net weight change was taken as the amount of moisture absorbed by each getter material.

In a separate test, the ratio of gas space to getter sample (0% rated capacity) was scaled to that anticipated for deployment in the TRUPACT-II ICV. The samples in the gas manifold were equilibrated with room air. Then successive aliquots of hydrogen (≈ 5 to 10%) were added to the sample in air until the total pressure drop indicated all of the oxygen and excess hydrogen were consumed. Each sample was then visually examined to determine if liquid water was present.

Compatibility

Compatibility of the getter must be ensured with respect to the chemical contents of the payload and the materials of construction of the TRUPACT-II. CMH getters are made of stable, inorganic materials similar to those listed in Tables A-2 through A-6 of the Statement of Work and compatibility problems are not anticipated. Similarly, no potential incompatibilities are anticipated for VEI polymer getter, with the possible exception of nitrate salts. However, the polymer getter should be no more reactive toward the nitrate salts than are other organic materials in the waste. It is not

clear at this time what is the actual potential for getter deployed in the ICV to have physical contact with or otherwise to be exposed to non-gaseous chemical contents of the payload. Therefore, with the exception of the evaluation of pyrophoricity described below, additional tests were deferred until appropriate compatibility tests can be defined.

Because some metal hydrides are known to be pyrophoric, a screening test was conducted with LANAI SGMH to evaluate its potential for pyrophoric behavior. A 2.0-g sample of LANAI SGMH was loaded to 100% of its useful capacity and the excess hydrogen evacuated from the chamber. The sample chamber was then rapidly equilibrated with room atmosphere and then sealed. Temperature and pressure inside the sample chamber were monitored for any indication of vigorous exothermic reaction. The test was repeated with the sample saturated with hydrogen. No significant increase in either temperature or pressure was recorded in either case. A similar test was conducted for VEI getter, although the manufacturer's material safety data sheet indicates that it can be stored and handled safely in air. Again, no measurable increase in temperature or pressure was observed.

Temperature Effect from Getter

The SOW requires that the heat of reaction for the getter/hydrogen reaction be provided in Watts per mole (W mol^{-1}) of hydrogen. No experimental work is necessary. The heat of reaction for hydrogen absorption by the metal hydride has already been measured at 30 kcal mol^{-1} of hydrogen. Under worst-case conditions, assuming only recombination, the heat of reaction is 68 kcal mol^{-1} of hydrogen. Using the maximum hydrogen generation rate for the ICV of $1.2 \times 10^{-5} \text{ mol s}^{-1}$ for 60 days, the calculated heat generation for LANAI SGMH is 0.024 W mol^{-1} for hydrogen absorption and 0.054 W mol^{-1} for the recombination reaction (worst-case). Similarly, the maximum heat of reaction for VEI getter is 0.024 W mol^{-1} of hydrogen when functioning as a getter and 0.054 W mol^{-1} when functioning as a recombiner.¹⁶ Therefore, the maximum heat production for either getter would be: $0.054 \text{ W mol}^{-1} \times 62 \text{ mol} = 3.4 \text{ W}$.

Passive versus Active Getter Systems

No testing is necessary because both LANAI SGMH and VEI getter are passive systems and require no external energy source.

Radiation Effects on Getter

Radiation effects need not be tested because the getter will be placed inside the ICV. However, because VEI getter is planned for use at the SRS for transportation of radioactive materials, the effects of exposure to gamma radiation on getter performance were investigated. Radiolytic decomposition of the unsaturated organic polymers could potentially result in decreased hydrogenation rate or hydrogen capacity. However, in our tests no effects on getter performance (rate or capacity) were noted after exposure to up to 100,000 R from cobalt-60. For the TRUPACT-II application, there are no other likely mechanisms for decreasing VEI getter capacity.

Results and Discussion

Operating Temperature Range

In general, the kinetics of hydrogen absorption and hydrogenation reactions decreases with temperature and reactant concentration (i.e., hydrogen pressure and available getter capacity). However, in the case of metal hydrides and composite metal hydrides, the equilibrium hydrogen pressure also decreases as temperature decreases. [In contrast to the effect of decreasing temperature on absorption kinetics, this reduction in equilibrium pressure tends to enhance the hydrogen absorption rate.] In addition, the hydrogen absorption and hydrogenation rates are reduced by the presence of inert gases (e.g., nitrogen or helium) which slow hydrogen molecules from reaching the getter material due to an increase in molecular collisions.

Figure 3 is a plot of LANA1 SGMH hydrogen absorption rate, at three different temperatures, as a function of hydrogen concentration in nitrogen. The rates at 70 °F and –20 °F are essentially the same, decreasing from about $8 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 5% (≈ 30 torr) hydrogen to less than $2 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 1% (≈ 5 torr) hydrogen. The rate at 160 °F (lower solid line) is from 1.5 to 2 times lower. This decrease in rate is attributed to the corresponding increase in equilibrium hydrogen pressure that offsets the expected increase in absorption kinetics with temperature. In comparison, the rate of hydrogen absorption (not plotted) for the same sample at 70 °F and approximately 30 torr hydrogen in vacuum (100% hydrogen) was $7 \times 10^{-4} \text{ mol s}^{-1} \text{ kg}^{-1}$, or about 100 times greater. Thus, the decrease in hydrogen concentration by dilution in nitrogen has a much greater impact on rate than does temperature for the range of –20 °F to 160 °F.

Also shown in Figure 3 is the rate of hydrogen removal in air for LANA1 SGMH at –20 °F in the range of 4 to 5 vol % hydrogen. A decrease in rate from $8 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ for hydrogen in nitrogen to $1 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ for hydrogen in air was observed. However, this decrease may be attributed

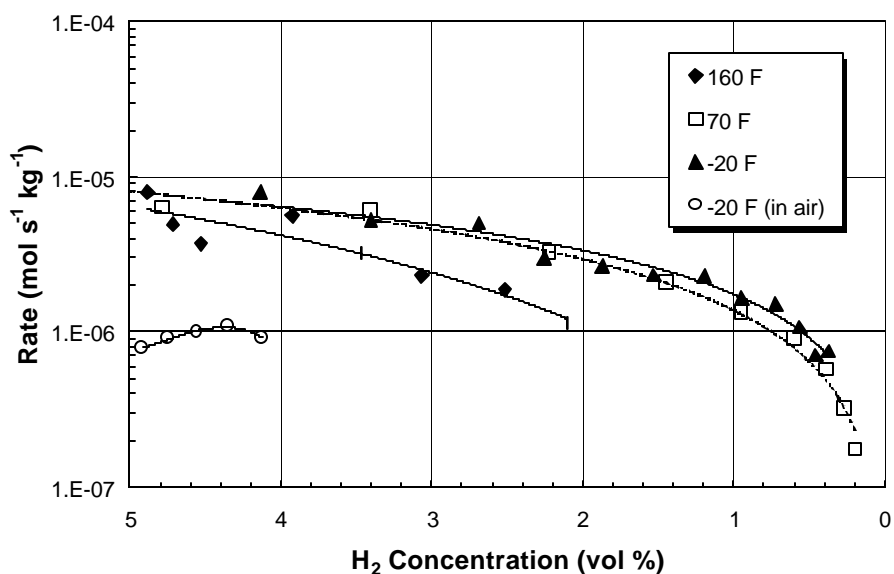


Figure 3. Rate of hydrogen absorption in nitrogen by LANA1 SGMH for the anticipated operating temperature range of the TRUPACT-II ($P_{N_2} \approx 525$ torr at 70 °F).

primarily to the effect of air on getter performance because the hydrogen removal rate in air at 70 °F is on the order of $2 \text{ to } 3 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$. Therefore, using the minimum amount of LANA1 SGMH based on capacity (i.e., 140 kg), an overall hydrogen removal rate of at least $1 \times 10^{-4} \text{ mol s}^{-1}$ at 4% hydrogen could be maintained at -20 °F in air.

Figure 4 shows the rate of hydrogenation for VEI getter as a function of hydrogen concentration in nitrogen (or air) at several different temperatures. The rates at 160 °F and 70 °F are similar, decreasing from approximately $2 \times 10^{-5} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 5% hydrogen to less than $5 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 1% hydrogen. The rate in nitrogen or air at 3 °F is about two to three times lower.[†] In contrast, the hydrogenation rate at 15 torr of hydrogen in vacuum (not plotted) decreased from 7×10^{-4} to $7 \times 10^{-5} \text{ mol s}^{-1} \text{ kg}^{-1}$ when the temperature was decreased from 79 °F to 27 °F. Therefore, dilution of hydrogen from a concentration of 100% (in vacuum) to 5% in nitrogen had a greater impact on rate than the change in temperature from 160 °F to 3 °F.

The rates in nitrogen at -10 °F and -20 °F are about 6×10^{-7} and $4 \times 10^{-7} \text{ mol s}^{-1} \text{ kg}^{-1}$, respectively. The abrupt tenfold decrease in hydrogenation rate over this small temperature (13 °F) range was unexpected, and this apparent discontinuity in the relationship between temperature and rate needs to be investigated in more detail. Even so, based on current rate measurements at -20 °F, only about 30 kg of getter would be required to remove hydrogen from the ICV at the maximum expected generation rate of $1.2 \times 10^{-5} \text{ mol s}^{-1}$. This amount of getter is 2.3 times greater than the 13 kg of getter required based on capacity. Thus, at the low temperature extreme, the amount of VEI getter required to meet the SOW requirements is determined by rate of hydrogen removal, not hydrogen capacity. [Note: At 3 °F the overall hydrogen removal rate for 13 kg of VEI getter is greater than $1.2 \times 10^{-5} \text{ mol s}^{-1}$, even at 1% hydrogen concentration.]

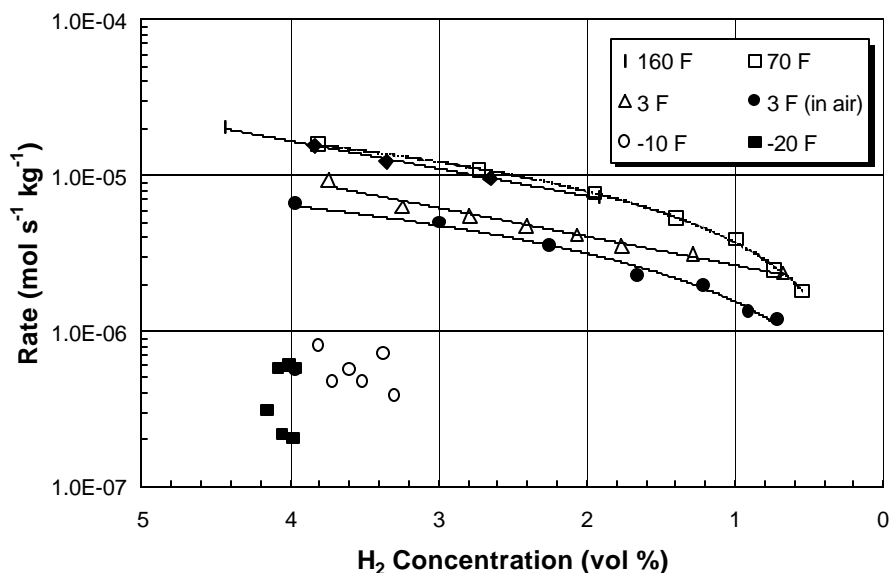


Figure 4. Hydrogenation rates in nitrogen for VEI polymer getter over the anticipated operating temperature range of the TRUPACT-II ($P_{N_2} \approx 525 \text{ torr}$ at 70 °F).

[†] The rates in nitrogen and air at 3 °F were determined for a sample of VEI getter saturated with water (i.e., $\approx 2 \text{ wt } \%$) to demonstrate that freezing of the water had no effect on getter performance.

Reversibility

Figure 5 compares the increase in total pressure when LANA1 SGMH and VEI getter, loaded to 100% of their rated capacities, were heated in a nitrogen atmosphere from 70 °F to 160 °F. As a control, the test was repeated for LANA1 SGMH after fully desorbing hydrogen from the sample by heating under vacuum. Therefore, the increase in pressure observed for the control sample is due solely to the increase in temperature. The difference in total pressure at 160 °F for LANA1 SGMH at 100% and 0% rated capacity was about 24 torr.[‡] This difference is equal to the amount of hydrogen that was desorbed upon heating and, therefore, is a measure of the reversibility of the hydrogen absorption reaction by LANA1 SGMH. This amount of hydrogen would be equivalent to about 3.2 vol % at a total pressure of one atmosphere. In the case of VEI getter, the total pressure at 160 °F was essentially the same as for the control sample, indicating no significant release of hydrogen. This result is not surprising because VEI getter reacts with hydrogen by an irreversible hydrogenation mechanism rather than the reversible hydriding mechanism for LANA1 SGMH.

Based on our tests, both getter materials tested satisfy the reversibility requirement for use in the TRUPACT-II. However, to promote diffusion of hydrogen gas from each drum into the ICV, it is desirable to maintain the hydrogen concentration as low as possible in the ICV. Our tests indicate that VEI getter is capable of maintaining the hydrogen concentration below 1 vol % even at the maximum operating temperature, thus maximizing diffusion of hydrogen from the drums into the ICV.

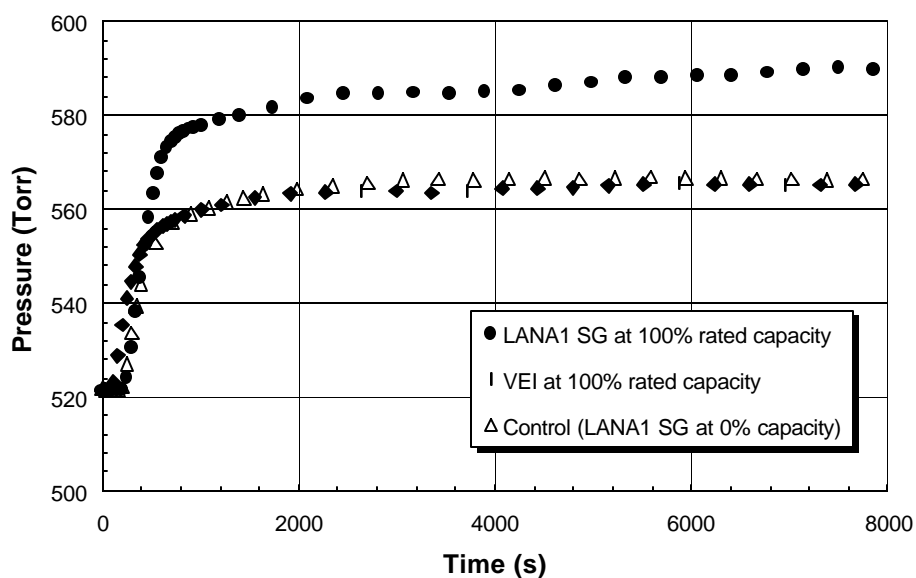


Figure 5. Desorption of hydrogen from LANA1 SGMH and VEI polymer getter when loaded to 100% of the rated capacity at 70 °F and then heated to 160 °F in a nitrogen atmosphere.

[‡] The fully loaded samples were also heated in vacuum with essentially the same results. That is, for LANA1 SGMH the pressure increased from about 1.5 torr to about 25 torr and for VEI getter the pressure increased from about 1.5 torr to about 3.9 torr.

Getter Operational Life (Capacity)

The change in hydrogen removal rate with increased hydrogen loading was measured to demonstrate the ability of each getter to maintain sufficient rate as capacity is consumed throughout the full 60-day shipping period. The hydrogen absorption rate in nitrogen for LANA1 SGMH as a function of hydrogen concentration at ambient temperature is shown in Figure 6. The rate was found to decrease from about $9 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 5% hydrogen to about $2 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 1% hydrogen for all three levels of getter loading (10%, 50%, and 90% rated capacity). [Note: As stated previously, the measured rates are for freshly activated sample not previously exposed to air or moisture. One possible option for minimizing the effects of air exposure will be presented at the conclusion of this report.]

Similarly, Figure 7 is a plot of the hydrogenation rate of VEI getter at ambient temperature as a function of hydrogen concentration in nitrogen at 5%, 50%, and 90% rated capacity. The rates at 5% and 50% rated capacity decrease from about $2 \times 10^{-5} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 5% hydrogen to about $4 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 1% hydrogen. When loaded to 90% rated capacity, the rate at 4% hydrogen drops to about $1 \times 10^{-5} \text{ mol s}^{-1} \text{ kg}^{-1}$, but it is still about $4 \times 10^{-6} \text{ mol s}^{-1} \text{ kg}^{-1}$ at 1% hydrogen. These tests show that both LANA1 SGMH and VEI getter maintain nearly constant hydrogen gettering rates for a given hydrogen concentration across the full range of their rated capacities. Therefore, the mass of getter required to meet the stated rate requirement of $1.2 \times 10^{-5} \text{ mol s}^{-1}$ is determined by factors other than the effect of loading.

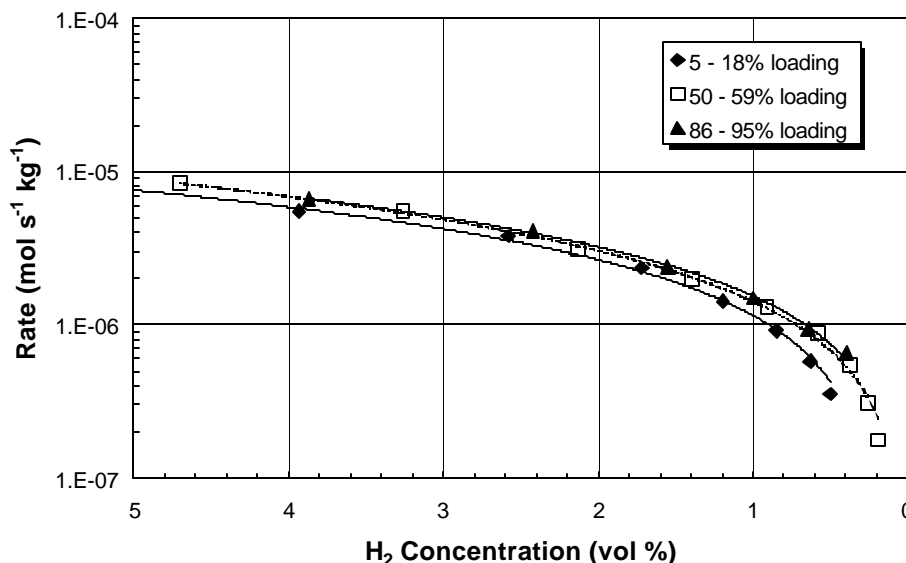


Figure 6. LANA1 SGMH absorption of hydrogen from nitrogen at ambient temperature at 10%, 50%, and 90% rated capacity.

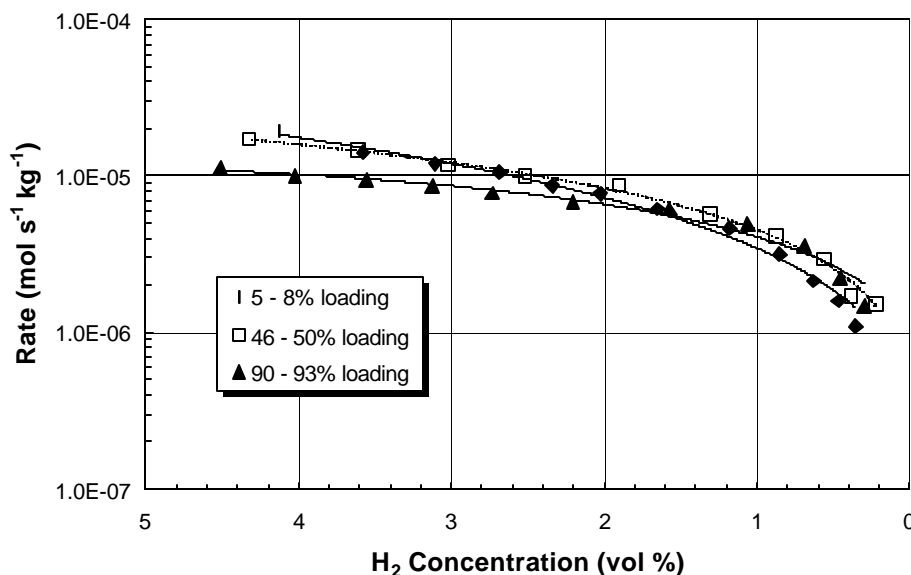


Figure 7. VEI polymer getter hydrogenation rates in nitrogen at ambient temperature at 5%, 50%, and 90% rated capacity.

Pressure

The effect of pressure on the rate of hydrogen removal for each getter is shown in Figures 8 and 9. In these graphs, rate is plotted as a function of hydrogen concentration at total pressures of 0, 15, and 50 psig (1.0, 2.0, and 4.4 atm). The plots in Figures 8 and 9 indicate faster initial rates and greater decreases in rate with decreasing hydrogen concentration than observed for other tests described in this report. The differences can be attributed to the manner in which the tests were conducted. In all other tests the nitrogen (or air) was introduced first, then hydrogen was added in a separate step, thus requiring some time for hydrogen to diffuse throughout the vessel and reach the getter.[§] In effect, until a homogeneous mixture was attained, the hydrogen concentration at the getter sample was less than the overall hydrogen concentration in the sample container. Therefore, the recorded hydrogen removal rate at the given initial hydrogen concentration (i.e., 5%) understates the actual rate at 5% hydrogen; thus, those test results provide a conservative estimate of getter performance.

In contrast, for this series of tests to evaluate pressure effects, a previously prepared, homogeneous mixture of hydrogen in nitrogen was added directly to the evacuated sample container. Because no time was required for gas mixing, the sample was exposed to the full hydrogen concentration immediately. Therefore, the rate vs. hydrogen concentration data plotted in Figures 8 and 9 more accurately reflect the actual hydrogen removal rates at a given hydrogen concentration because the hydrogen and nitrogen are well mixed.

In the case of LANA1 SGMH (Fig. 8), the rate at a given percentage hydrogen concentration increased by a factor of three to four as the total pressure was increased from 0 psig (initial $P_{H_2} \approx 40$ torr) to 50 psig (initial $P_{H_2} \approx 190$ torr). The variation in rate at a given percentage hydrogen

[§] In all cases, the hydrogen concentration was calculated using pressure-volume-temperature relationships.

concentration with total pressure was somewhat less for VEI getter (Fig 9). These tests demonstrate that both getters are capable of maintaining sufficient rate across the operating pressure range for the TRUPACT-II, and factors other than total pressure will determine the required amount of getter.

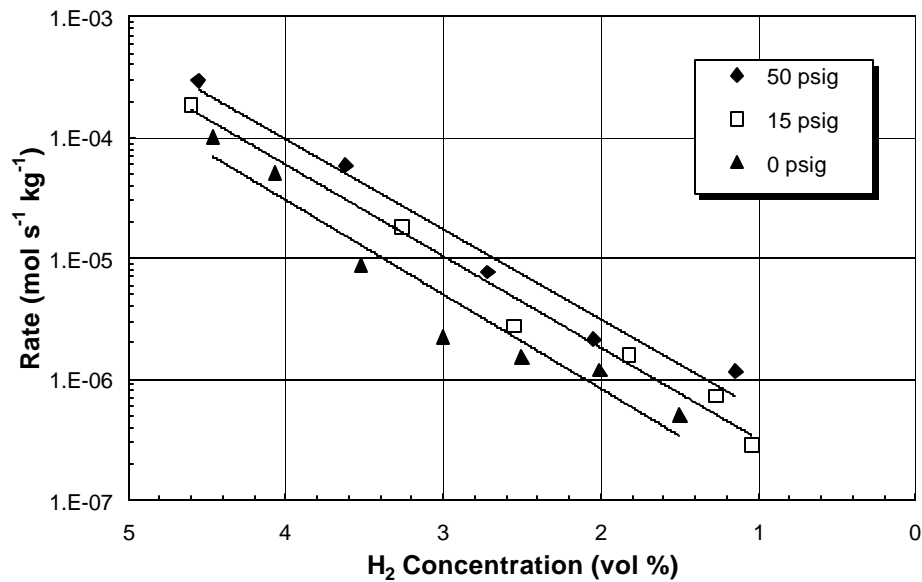


Figure 8. Effect of total pressure on LANA1 SGMH hydrogen absorption rate in nitrogen at ambient temperature as a function of hydrogen concentration.

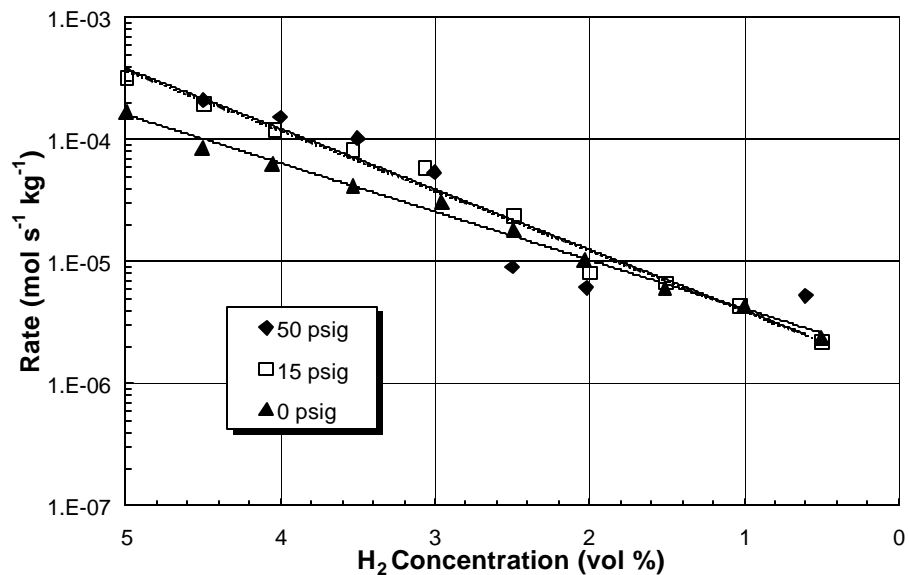


Figure 9. Effect of total pressure on VEI hydrogen gettering rate in nitrogen at ambient temperature as a function of hydrogen concentration.

Potential Poisons

The effect of potential poisons on hydrogen removal rates for LANA1 SGMH and VEI getter in both vacuum and nitrogen are summarized in Table 3. These data indicate that exposure to poisons (including air) had considerable effect on the hydrogen absorption rate of LANA1 SGMH, but negligible effect on VEI getter performance. The data from select poison tests are plotted in Figures 10 through 14. These figures show the moles of hydrogen absorbed or consumed per kilogram of getter over the time in seconds. The data are plotted in this fashion to show more clearly the impact of the various poisons on hydrogen absorption rate. In cases where a particular poison is not presented, the data for that poison are bounded by the plotted data. All tests were conducted at ambient temperature, and the initial hydrogen pressure was approximately 30 torr in each case.

Table 3. Summary of Poison Effects on Getter Performance

Poison	LANA1 SGMH H ₂ Absorption Rate (mol s ⁻¹ kg ⁻¹)		VEI Getter Hydrogenation Rate (mol s ⁻¹ kg ⁻¹)	
	In Vacuum	In N ₂	In Vacuum	In N ₂
	(25 to 30 torr H ₂)	(≈ 4% H ₂)	(25 to 30 torr H ₂)	(≈ 4% H ₂)
Control (Air)	1.3 x 10 ⁻⁷	1.1 x 10 ⁻⁶	1.1 x 10 ⁻³	9.0 x 10 ⁻⁶
Chloroform	8.1 x 10 ⁻⁸	Not measured	1.2 x 10 ⁻³	1.0 x 10 ⁻⁵
Tetrachloroethylene	5.2 x 10 ⁻⁸	4.5 x 10 ⁻⁷	9.3 x 10 ⁻⁴	7.3 x 10 ⁻⁶
Methanol	5.4 x 10 ⁻⁸	Not measured	1.0 x 10 ⁻³	9.9 x 10 ⁻⁶
Toluene	1.6 x 10 ⁻⁸	Not measured	9.5 x 10 ⁻⁴	8.4 x 10 ⁻⁶
Acetone	4.7 x 10 ⁻⁸	2.9 x 10 ⁻⁷	1.1 x 10 ⁻³	8.8 x 10 ⁻⁶
Hydrogen chloride	4.0 x 10 ⁻⁸	8.0 x 10 ⁻⁸	1.1 x 10 ⁻³	9.4 x 10 ⁻⁶
Carbon monoxide	5.0 x 10 ⁻⁸	5.2 x 10 ⁻⁸	1.1 x 10 ⁻³	1.1 x 10 ⁻⁵
Water vapor	Not Measured	6.6 x 10 ^{-7(a)}	Not Measured	9.6 x 10 ^{-6(b)}

^(a) The rate was measured after the sample absorbed 8.8 mg (0.44 wt %) of water over a period of about 15 days during the recombination experiment described in the section on Free Liquids. This amount of water would correspond to about 30,000 ppm of water vapor in one of the 360-mL poison test vessels.

^(b) The rate was measured after the sample was stored in air at 100% relative humidity until a constant weight was attained. The sample absorbed about 27 mg of water (2.4 wt %), which would correspond to approximately 93,000 ppm of water vapor in one of the 360-mL poison test vessels.

For LANA1 SGMH, the initial hydrogen absorption rates in vacuum following exposure to poisons were from two to eight times lower than the rate measured for the control sample, which was exposed only to air. Moreover, the initial rate in vacuum for the LANA1 SGMH control sample was over 5000 times lower than the rate in vacuum for a sample with minimal or no air exposure (about 7 x 10⁻⁴ mol s⁻¹ kg⁻¹). In general, the rates for LANA1 SGMH improved over time with continued exposure to hydrogen. When the hydrogen absorption tests were repeated in nitrogen, the observed rates were greater in every case compared to results from the tests in vacuum with the exception of the sample exposed to carbon monoxide. However, the rate in nitrogen for the control sample remained over five times lower than the rate in nitrogen for LANA1 SGMH with minimal or no air exposure. In contrast, the hydrogenation rates of VEI getter in both vacuum and nitrogen showed little or no effect from exposure to air or other potential poisons in these screening tests.

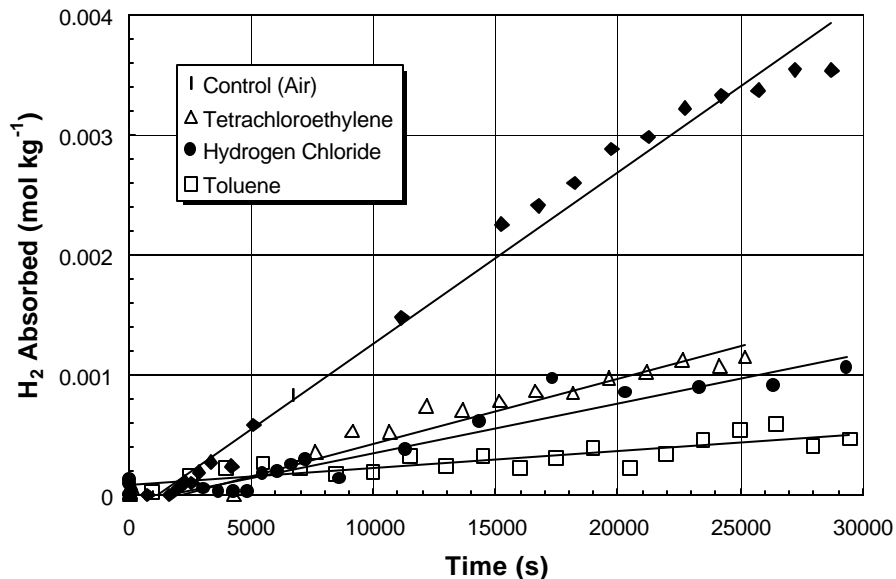


Figure 10. Effect of selected poisons on hydrogen absorption by LANA1 SGMH in vacuum (initial $P_{H_2} \approx 30$ torr).

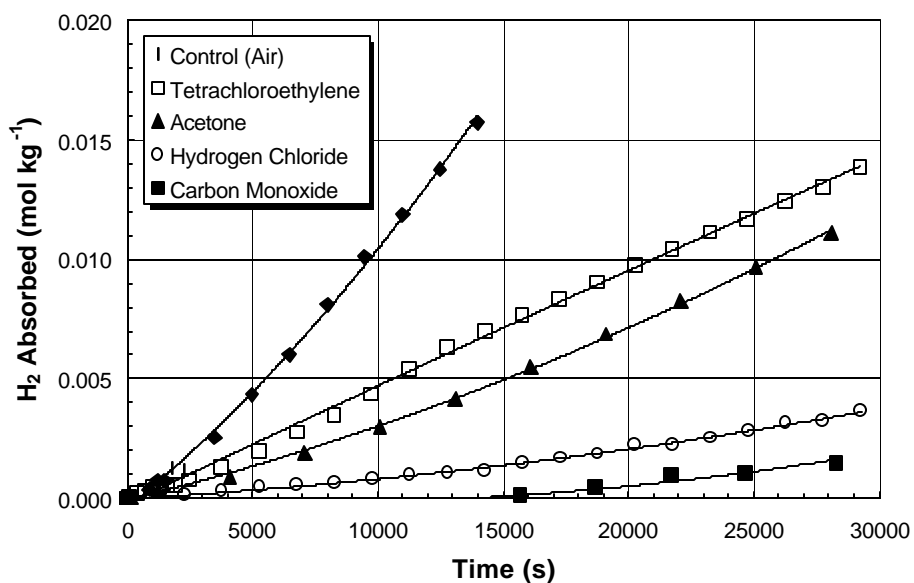


Figure 11. Effect of selected poisons on hydrogen absorption by LANA1 SGMH for 5% hydrogen in nitrogen gas mixture (initial $P_{H_2} \approx 30$ torr; initial $P_{tot} \approx 550$ torr).

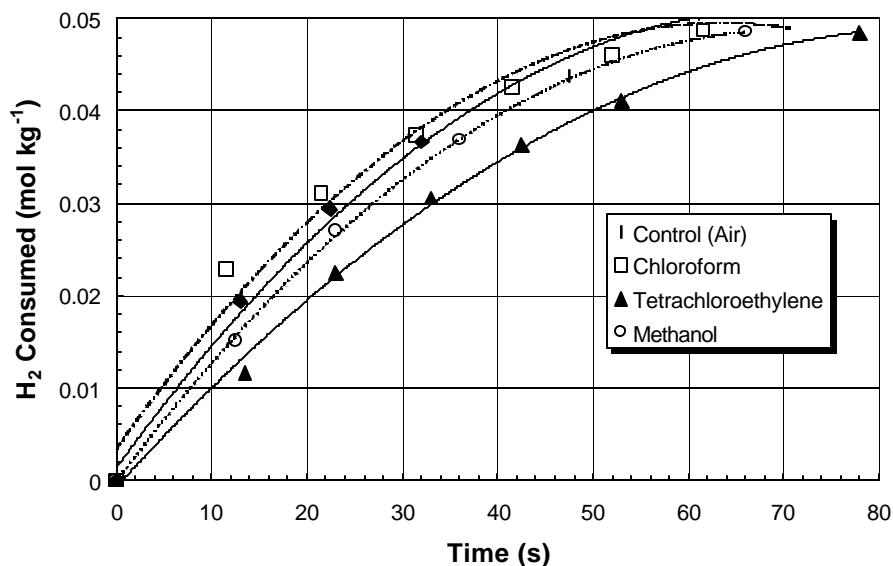


Figure 12. Effect of selected poisons on hydrogenation of VEI polymer getter in vacuum (initial $P_{H_2} \approx 30$ torr).

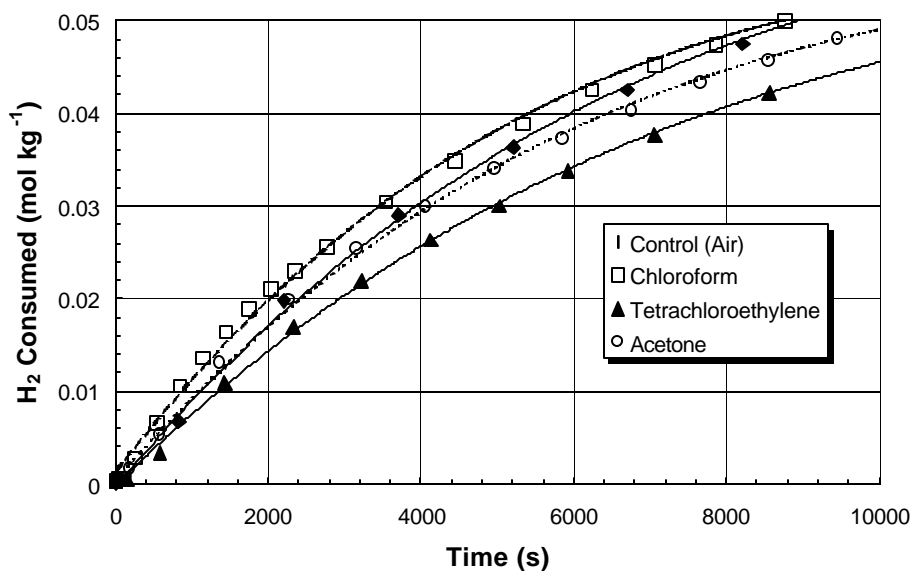


Figure 13. Effect of selected poisons on hydrogenation rate of VEI polymer getter for 5% hydrogen in nitrogen gas mixture (initial $P_{H_2} \approx 30$ torr; initial $P_{tot} \approx 550$ torr).

It is uncertain at this time what causes the decrease in LANA1 SGMH hydrogen absorption rate after exposure to air. Two possible explanations are (1) partial oxidation of the active metal surface due to incomplete protection from oxygen and (2) physical blocking of the silica matrix pores with molecules of oxygen and/or water. Despite the decrease in rate, evaluation of the hydrogen capacity for LANA1 SGMH following a weeklong exposure to 1000-ppm chloroform in air revealed no measurable loss of capacity. However, capacities were not measured for other samples following exposure to poisons, so we cannot state that capacity was unaffected in all cases. For VEI getter, the hydrogenation rates in vacuum and in nitrogen were essentially unaffected by air or other poisons.

Previous tests with composite metal hydrides indicated that the negative effects of air and/or moisture on CMH performance could potentially be reduced by mixing some zeolite with the CMH sample. To test this idea, the weeklong exposure of LANA1 SGMH to air was repeated with SGMH combined with two different amounts of zeolite (4A molecular sieve). Following the weeklong air exposures, the hydrogen absorption rates in vacuum for the combined SGMH/zeolite samples were determined as described for other poison tests and compared with that for the SGMH control sample with no zeolite (Fig. 14). Based on these test results, the hydrogen absorption rate after air exposure clearly improved for the SGMH samples combined with zeolite. The overall hydrogen removal rates after approximately 15,000 seconds were $1.5 \times 10^{-7} \text{ mol s}^{-1} \text{ kg}^{-1}$ for 2 g SGMH only; $3.4 \times 10^{-7} \text{ mol s}^{-1} \text{ kg}^{-1}$ for 2 g SGMH plus 0.5 g zeolite; and $6.1 \times 10^{-7} \text{ mol s}^{-1} \text{ kg}^{-1}$ for 2 g SGMH plus 2 g zeolite. Because the zeolite has a relatively high affinity for water, the observed improvements in rate with increasing zeolite content are probably due, at least in part, to reduced moisture absorption by SGMH. The zeolite would also tend to absorb a variety of poison vapors and therefore would help mitigate the effects of poisons on LANA1 SGMH.

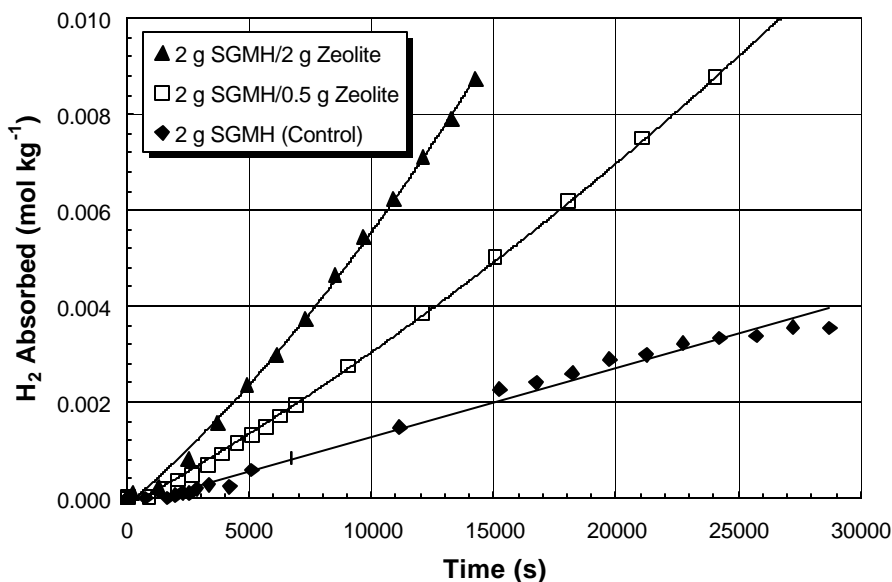


Figure 14. Comparison of LANA1 SGMH hydrogen absorption rates in vacuum following exposure to air for one week with and without zeolite present.

Free Liquids

In Figure 15 the amount of moisture absorbed by each getter when stored at ambient temperature and 100% relative humidity is plotted as a function of time. LANA1 SGMH was found to absorb almost 30 wt % moisture over a period of about 25 days. The relatively high capacity of SGMH for water is due to the very hydrophilic nature and porous structure of the sol-gel matrix. Thus, any water formed from recombination of hydrogen and oxygen by LANA1 SGMH would be readily absorbed by the getter matrix. The fact that no free liquid was observed in the sample container following the scaled recombination experiment supports this conclusion.

In contrast, VEI polymer getter is quite hydrophobic and was found to absorb a maximum of only 2.4 wt % moisture in about 20 days. In addition, following the scaled recombination experiment described previously, a small amount of condensed moisture was observed on the walls of the sample vial. However, the formation of free liquid water from recombination can easily be prevented by combining a small amount of zeolite sufficient to absorb the maximum expected amount of water. This experiment was repeated with a small amount of 4A molecular sieve added to the VEI getter sample vial, and no free liquid was observed once all of the oxygen had been consumed. Therefore, the generation of free water from recombination of hydrogen and oxygen is not anticipated to be a concern for either getter material.

As previously stated in the section on operating temperature range, we have also measured the rate of hydrogen removal in nitrogen and in air at low temperature (3 °F) for VEI getter saturated with water. Our test results indicated that freezing of the water had no effect on getter performance.

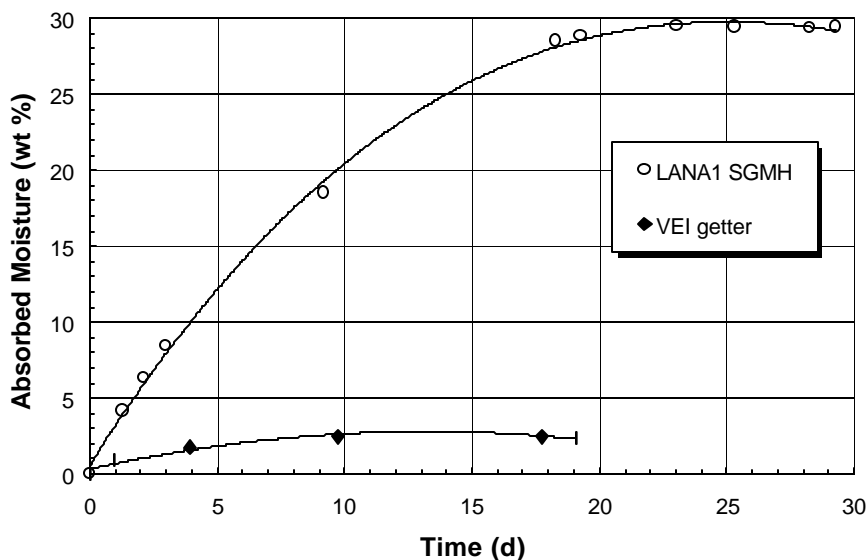


Figure 15. Moisture uptake by SGMH and VEI getter when stored at ambient temperature and 100% relative humidity.

Summary of Hydrogen Getter Test Data

The results of Phase 1 testing demonstrate that both LANA1 SGMH and VEI polymer getter can potentially meet the requirements for use in the TRUPACT-II. However, VEI getter exhibits a number of advantages over LANA1 SGMH with regard to hydrogen gettering rate and capacity. These advantages are: (1) a useful (rated) hydrogen capacity over 10 times greater than for LANA1 SGMH; (2) the ability to maintain a much lower hydrogen concentration at the maximum operating temperature of the TRUPACT-II; and (3) a much greater resistance to potential poisons, including air and water vapor.

As discussed previously, we originally planned to test two additional composite metal hydrides (LANA1 CMH and NdCo_3 CMH) that showed promise in early screening tests. Although our initial attempt to scale-up production of these materials was unsuccessful, it should be feasible to prepare them on a larger scale. Because NdCo_3 exhibits significantly lower equilibrium hydrogen pressures than does LANA1, NdCo_3 CMH offers the possibility for improved hydrogen capacity and lower hydrogen concentrations at elevated temperature (i.e., 160 °F) compared to LANA1 SGMH. In addition, it appears likely that the effects of poisons on composite metal hydrides can be reduced by the addition of zeolite to the getter package. Therefore, NdCo_3 CMH combined with zeolite could potentially compare more favorably with VEI getter than did LANA1 SGMH. Nevertheless, based on our test results, VEI getter is the better choice at this time because it meets all of the SOW requirements in its currently manufactured form.

During tests to evaluate pressure effects, an approximate tenfold increase in initial hydrogen removal rate (i.e., at approximately 5 vol % hydrogen) was observed compared to initial rates recorded during other tests. The difference was attributed to the manner in which the hydrogen was introduced to the sample. In the tests to evaluate pressure effects, a homogeneous gas mixture of approximately 5% hydrogen in nitrogen was added to the sample container. In other tests, a small quantity of hydrogen was added to nitrogen (or air) already present in the sample container, in which case some time was required for the gases to mix completely. Therefore, when hydrogen was added to nitrogen or air already present, estimates of initial hydrogen removal rates were conservative by a factor of five to ten. These observed differences in rate based on the manner in which hydrogen was introduced to the sample serve to point out the importance of geometry (i.e., getter deployment location) and necessity of full-scale testing of getter function prior to implementation.

With very few exceptions, the hydrogen removal rates measured for VEI getter at a given hydrogen concentration in nitrogen (or air) were found to be relatively constant across a broad range of operating conditions and available getter capacity. In fact, for temperatures above 3 °F, 13 kg of VEI getter are sufficient to meet the capacity requirement while maintaining a hydrogen removal rate at least 10 times greater than required. However, at temperatures below 3 °F, the rate was found to decrease by a factor of 30 to 50 at 4% hydrogen. Although we are not certain at this time why the rate decreased so dramatically, it is likely related to the temperature dependence of hydrogen dissociation by the palladium catalyst. It is unlikely to be related to any fundamental changes in the polymers that make up the getter because such changes occur at temperatures much lower than -20 °F.¹⁶ If the decrease in rate is due to temperature dependence of the catalyst, it can be addressed most simply by increasing the palladium content of the polymer getter. As stated previously, however, even at -20 °F only about 30 kg of VEI getter are required to meet the SOW rate requirement at a hydrogen concentration of 4%.

Our poison screening tests indicate that the performance of VEI polymer getter is unlikely to be affected by poisons at the concentrations expected for the TRUPACT-II. Nevertheless, we recognize

that additional tests are needed to determine at what level, if any, potential poisons may impact the getter performance. In addition, these tests need to be conducted in the presence of hydrogen to provide a better simulation of the actual conditions for use in the TRUPACT-II.

Comparison of Getter Candidates

The results of this effort have demonstrated two potential materials for mitigating the build-up of hydrogen gas in the TRUPACT-II ICV. The first material proposed for this application, in response to the TMFA request for proposals, was LANA1 SGMH. Subsequently, the VEI polymer hydrogen getter was identified as a good candidate for use in this type of application. VEI getter has been evaluated at SRS in a parallel effort to support on-site transportation of legacy nuclear materials in a much smaller shipping package (i.e., a 4-L ICV volume and 35-gal overpack). The results of both efforts were presented in this document and will be used to compare the efficacy of these options for future use in the TMFA's Hydrogen Gas Getters program.

In a previous effort,⁹ we proposed 10 criteria for ranking the potential of a getter material for use in radioactive material transportation. These criteria include:

1. Cost
2. Availability
3. State of Development
4. Recyclability
5. Capacity
6. Weight
7. Heat Production
8. Kinetics
9. Simplicity of Design
10. Ease of Handling/Storage

Using these same criteria to compare VEI and SGMH supports our decision making process and leads to a recommendation for Phase 2 enhancements and additional testing.

Cost and Availability

The VEI getter material evaluated as part of this test program is commercially available in large quantities for about \$700 per kilogram. Up to about one-half of this cost may be attributed to the palladium content of the getter. With the potential need to deploy about 30 kg of VEI getter (based on the rate at -20 °F) with only half of the capacity being consumed, it is reasonable to consider increasing the palladium content to optimize price and reduce the getter volume. Nevertheless, using VEI getter could cost \$10,000 to \$20,000 per TRUPACT-II neglecting recovery of the palladium catalyst.

The cost of VEI getter must be compared with the cost and effort required to scale-up LANA1 SGMH production, regeneration, and recertification of the getter assembly after each use. The initial cost of metal hydride and SGMH production and maintenance facilities could be amortized over the life of the SGMH assembly. There is no current commercial application for SGMH so the cost for material production facilities, scale-up of production, etc. will need to be paid for by this single application. The risk associated with determining the SGMH assembly lifetime and ongoing recertification to meet operating requirement needs also to be factored into the cost evaluation.

Because VEI getter is produced in large batches and is commercially available, there is minimal risk associated with selection of this material. Much of the economic value of the palladium catalyst can be recovered and the palladium used in production of new getter. This recycling avoids issues with materials lifetime and maintenance costs found with SGMH. VEI getter meets the proposed requirements as currently manufactured at a price that does not seem cost prohibitive based on the expected increase in TRUPACT-II wattage. Based on cost and availability, VEI getter is the better candidate for Phase 2 improvements and additional testing to support a getter system design.

State of Development

The results of the tests documented as part of this report suggest that VEI getter meets all of the SOW requirements. The work with SGMH shows that it is much more sensitive to poisons (including air and water vapor) than is VEI getter. Efforts to improve the use of metal hydrides resulted in a product that requires additional effort to successfully scale-up to even the 100-g batch size. Therefore, VEI getter is currently better able to meet the requirements for use in the TRUPACT-II.

Recyclability

Recyclability is primarily important to the economics of using a particular getter product. As such, this issue was addressed as part of the Cost and Availability discussion.

Capacity and Weight

Based on the results of tests documented in this report, about 140 kg of SGMH will be required to meet TRUPACT-II hydrogen getter capacity requirements. However, as much as 750 kg may be required based on our evaluation of potential poison effects. In contrast, only 30 kg of VEI getter are required to meet the hydrogen absorption rate under worst case conditions (i.e., -20 °F), and this amount will provide about twice the necessary capacity. Based on this data, VEI getter is the better performer in terms of capacity and weight.

Heat Production

Recombination of hydrogen and oxygen to generate water and absorption of this water on a molecular sieve or sol-gel material produces the maximum heat generation. When the getter materials are operated in a nitrogen environment, the resulting heat generated drops by about fifty percent. Both materials are expected to generate similar amounts of heat when operated in air or nitrogen. Consequently, the use of either material will affect TRUPACT-II wattage in the same manner, so heat production does not influence the selection between SGMH or VEI getter.

Kinetics

The kinetics of hydrogen removal is a factor in determining the quantity of getter required. As such, this factor has been addressed as part of the evaluation of weight and capacity.

Simplicity and Ease of Handling

VEI getter is currently produced as a coarse powder and SGMH is produced as small pellets. Neither material presents any significant difficulties with regard to handling. In its current state of development, SGMH is sensitive to air and/or moisture and may require controls to prevent excessive moisture absorption. VEI getter is not particularly sensitive to the handling environment and functions very well after exposure to humid conditions. Future enhancement of VEI getter should

address changing the material form to small pellets to improve gas circulation. Based on the SGMH sensitivity to moisture, VEI getter will be easier to handle and will assure anticipated performance when installed in the TRUPACT-II. Therefore, the better candidate for Phase 2 testing in this category is VEI getter.

Conclusions

This comparison of LANA1 SGMH and VEI polymer getter shows that VEI getter is better or equivalent to LANA1 SGMH in every category. Based on the results of Phase 1 tests and a side-by-side comparison of the results, we recommend that Phase 2 of the TMFA effort focus on improvements to VEI getter. Phase 2 should also address any additional testing deemed important to development of a getter system in preparation for full-scale testing of a hydrogen getter assembly. Recommended efforts include:

1. optimization of the palladium catalyst content,
2. evaluation of poison effects in the presence of hydrogen,
3. manufacturing in pellet form to improve handling, and
4. understanding better the effect of temperature on material performance, particularly at or near the lower limit of -20°F .

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Appendix: Test Matrix

Evaluate Operating Temperature and Pressure range

Temperature

The hydrogen removal rate in nitrogen was measured at approximately 50% loading and a total pressure of about 0.7 atm.

	Rate at 4% H ₂ (mol s ⁻¹ kg ⁻¹)			
	-20 °F	3 °F	70 °F	160 °F
LANA1 SGMH	6.4 x 10 ⁻⁶	Not Measured	6.4 x 10 ⁻⁶	4.2 x 10 ⁻⁶
VEI getter	4 x 10 ⁻⁷	1.0 x 10 ⁻⁵	1.7 x 10 ⁻⁵	1.7 x 10 ⁻⁵

Pressure

The hydrogen removal rate in nitrogen was measured at approximately 50% loading and ambient temperature.

	Rate at 4% H ₂ (mol s ⁻¹ kg ⁻¹)		
	0 psig	15 psig	50 psig
LANA1 SGMH	3.1 x 10 ⁻⁵	6.0 x 10 ⁻⁵	9.5 x 10 ⁻⁵
VEI getter	6.5 x 10 ⁻⁵	1.2 x 10 ⁻⁴	1.2 x 10 ⁻⁴

Absorption Reaction Reversibility

Each getter sample was loaded to 100% rated capacity in nitrogen at ambient temperature and the initial pressure was recorded. Then each sample was heated in a fixed volume to 160 °F and the final pressure was recorded.

	P _{tot} at Equilibrium (torr)		P _{H2} at 160 °F (torr)	%H ₂
	70 °F	160 °F		
LANA1 SGMH	523	590	24	4.1
VEI getter	521	565	-1	0
Control (N ₂ only)	522	566	-	-

Getter Operational Life (Capacity)

The hydrogen removal rate in nitrogen ($P_{\text{tot}} \approx 0.7$ atm) was measured for each getter at approximately 5, 50, and 90% rated capacity and ambient temperature.

% Loading	Rate at 4% H ₂ (mol s ⁻¹ kg ⁻¹)		
	5%	50%	90%
LANA1 SGMH	5.9×10^{-6}	6.9×10^{-6}	6.9×10^{-6}
VEI getter	1.8×10^{-5}	1.6×10^{-5}	1.0×10^{-5}

Potential Poisons

Samples of each getter were exposed to poison vapor at a concentration of approximately 1000 ppm in a volume of about 360 mL for one week. Then, the hydrogen removal rate in vacuum, and in some cases nitrogen, was measured at ambient temperature for each sample.

Poison	LANA1 SGMH H ₂ Absorption Rate (mol s ⁻¹ kg ⁻¹)		VEI Getter Hydrogenation Rate (mol s ⁻¹ kg ⁻¹)	
	In Vacuum (25 to 30 torr H ₂)	In N ₂ (4% H ₂)	In Vacuum (25 to 30 torr H ₂)	In N ₂ (4% H ₂)
Control (Air)	1.3×10^{-7}	1.1×10^{-6}	1.1×10^{-3}	9.0×10^{-6}
Chloroform	8.1×10^{-8}	Not measured	1.2×10^{-3}	1.0×10^{-5}
Tetrachloroethylene	5.2×10^{-8}	4.5×10^{-7}	9.3×10^{-4}	7.3×10^{-6}
Methanol	5.4×10^{-8}	Not measured	1.0×10^{-3}	9.9×10^{-6}
Toluene	1.6×10^{-8}	Not measured	9.5×10^{-4}	8.4×10^{-6}
Acetone	4.7×10^{-8}	2.9×10^{-7}	1.1×10^{-3}	8.8×10^{-6}
Hydrogen chloride	4.0×10^{-8}	8.0×10^{-8}	1.1×10^{-3}	9.4×10^{-6}
Carbon monoxide	5.0×10^{-8}	5.2×10^{-8}	1.1×10^{-3}	1.1×10^{-5}
Water vapor	Not Measured	$6.6 \times 10^{-7(a)}$	Not Measured	$9.6 \times 10^{-6(b)}$

^(a) The rate was measured after the sample absorbed 8.8 mg of water over a period of about 15 days during the recombination experiment described below. This amount of water would correspond to about 30,000 ppm of water vapor in one of the 360-mL poison test vessels.

^(b) The rate was measured after the sample was stored in air at 100% relative humidity until a constant weight was attained. The sample absorbed about 27 mg of water, which would correspond to approximately 93,000 ppm of water vapor in one of the 360-mL poison test vessels.

Demonstrate the Absence of Free Liquids

A sample of each getter was stored in air at ambient temperature and 100% relative humidity until a constant weight was obtained.

	% Weight Gain
LANA1 SGMH	29.4
VEI getter	2.4

The ratio of gas space to getter sample was scaled to that anticipated for deployment in the TRUPACT-II ICV. The samples in the gas manifold were equilibrated with room air. Then successive aliquots of hydrogen (≈ 5 to 10%) were added to the sample in air until the total pressure drop indicated all of the oxygen and excess hydrogen were consumed. Each sample was then visually examined to determine if liquid water was present.

	Observation
LANA1 SGMH	No free liquid observed
VEI getter	Some condensed moisture on walls of vial
VEI/Molecular Sieve	No free liquid observed